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Fabrication of Transparent PbTiO_3 Glass-Ceramics

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Transparent high permittive glass-ceramics are of interest for electro-optic and electro-luminescent applications. A method for fabricating glass-ceramics of this type by crystallization of glasses in the $\text{PbO} \cdot \text{TiO}_2$ - $\text{AlO}_{1.5}$ - SiO_2 system was investigated. Transparent glass-ceramics consisting primarily of a large amount of ferroelectric PbTiO_3 crystals with a perovskite-type structure were obtained from the composition region with $\text{PbO} \cdot \text{TiO}_2 / (\text{AlO}_{1.5} + \text{SiO}_2) = 2$ and $1 \leq \text{AlO}_{1.5} / \text{SiO}_2 \leq 2.3$ in mole ratio. When a glass of the composition in the restricted region described above was heated from room temperature at a rate of $48^\circ\text{--}300^\circ\text{C/hr}$, a metastable liquid-liquid phase separation first occurred, and as the results, the homogeneous structure of the glass changed into a microheterogeneous structure composed of glassy droplets of 16–18 nm in diameter. At higher temperatures, the phase-separated glass transformed into transparent glass-ceramics consisting primarily of PbTiO_3 crystals each having a diameter almost the same as that of the glassy droplets precursorily formed. It was assumed that precipitation of very-fine-grained PbTiO_3 crystal of a perovskite-type in the glass was assisted by the metastable phase separation in very fine scales, which had occurred precursorily.

I. INTRODUCTION

Transparent high-permittive glass-ceramics are of high promises for electro-optic and electro-luminescent applications. Therefore, heretofore, many glass-ceramics of this type, consisting, for example, of NaNbO_3 ¹⁾, $(\text{Ba}, \text{Pb})\text{Nb}_2\text{O}_6$ ¹⁾, BaTiO_3 ¹⁾, and LiTaO_3 ²⁾ crystals, respectively, have been produced by way of experiment. The purpose of the present work is to explore the conditions for fabricating transparent glass-ceramics primarily of PbTiO_3 crystals of a perovskite-type by crystallization of glasses in the $\text{PbO} \cdot \text{TiO}_2$ - $\text{AlO}_{1.5}$ - SiO_2 system.

Process of crystallization of some glasses in the $\text{PbO} \cdot \text{TiO}_2$ - $\text{AlO}_{1.5}$ - SiO_2 system as well as properties of the resulting glass-ceramics have been reported by several researchers.^{3~9)} Their researches, however, did not deal with transparency of the glass-ceramics.

II. EXPERIMENTAL METHOD

1. Determination of Glass-Forming Region

Batches of various compositions in the $\text{PbO} \cdot \text{TiO}_2$ - $\text{AlO}_{1.5}$ - SiO_2 system were prepared from reagent grade Pb_3O_4 , TiO_2 , $\text{Al}(\text{OH})_3$ and SiO_2 . The batches were melted in Pt10%Rh crucibles of 50 cc capacity each covered with a Pt lid in a furnace electrically heated with SiC elements at 1350°C for about one hour. The melts were poured onto a steel plate, pressed into plates approximately 1 mm thick and immediately transferred into another furnace for annealing; *i.e.*, they were first

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heated at 500°C for 30 min and, after the furnace was switched off, allowed to cool in the furnace. The annealed glasses were examined visually and classified into three groups, one forming clear glasses, one devitrifying partially on cooling, and one devitrifying fully on cooling.

2. Heat Treatment of Glasses

Specimens with dimensions of 5–10 by 5–10 by 1 mm, were cut out from the annealed plates of the two groups; one forming clear glass and another devitrifying partially. From the latter only clear glassy portions were used as the specimens. They were placed on a Pt plate and subjected to the following heat treatments:

- (a) Heated from room temperature to a given temperature in a range from 500° to 1100°C within about one min by inserting the specimen rapidly into a furnace previously kept at the temperature described above and, after kept for one min in the furnace, taken out from the furnace to be allowed to cool in air.
- (b) Heated in a furnace from room temperature to a given temperature in a range from 500°–1100°C at a rate of 48°–300°C/hr, then immediately taken out from the furnace to be allowed to cool in air.

3. Investigation of Crystallization Process of Glasses

Two glass specimens, glasses 1 and 4 given in Table I, were heated from room temperature to various temperatures at a rate of 48°C/hr, and immediately taken out from the furnace. X-ray diffraction analyses were made of these heat-treated specimens to identify the crystal phases precipitated and to determine their total amounts and the size of each crystal. When only PbTiO_3 crystals of a perovskite-type precipitated in the specimen, their total amount was determined from the intensity of X-ray scattering due to residual glassy phase by the method reported by Ohlberg *et al.*¹⁰⁾ When another kind of crystals coprecipitated with the PbTiO_3 crystals, the amount of the coprecipitated crystals was calculated by subtracting the amount of PbTiO_3 crystals determined from the intensity of X-ray diffraction peak of the PbTiO_3 crystals from the total amount of all the crystals determined from the intensity of X-ray scattering due to the residual glassy phase. The grain size of the PbTiO_3 crystals was determined from the width of X-ray diffraction peak for the PbTiO_3 crystal, which had been extracted from the heat-treated specimens by immersion of the specimens in 5% HNO_3 at 90°C. Generally crystals precipitated in glasses are under mechanical stress, and the stress affects the width of X-ray diffraction peak for the crystals. The crystals were extracted from the heat-treated specimens so as to remove this stress. The extraction procedure was described in detail elsewhere.⁸⁾

III. RESULT AND DISCUSSION

1. Glass-Forming Region

Glass-forming tendency of the melts in the $\text{PbO} \cdot \text{TiO}_2$ - $\text{AlO}_{1.5}$ - SiO_2 system is shown in Fig. 1. The compositions of the melts, which form clear and partially

Transparent PbTiO₃ Glass-Ceramics

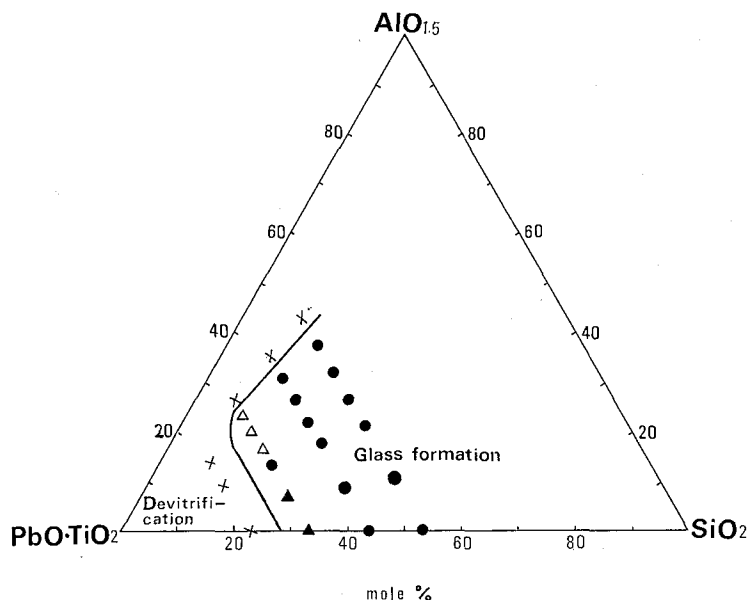


Fig. 1. Glass-forming tendency of melts and transparency of glass-ceramics obtained by heating at a rate of 48°–300°C/hr.

- ; Clear glass. Its glass-ceramic was opaque.
- △; Partially devitrified glass. Its glass-ceramic was transparent.
- ▲; Partially devitrified glass. Its glass-ceramic was opaque.
- ×; Fully devitrified glass.

devitrified glass on cooling, lie in a region restricted by the PbO·TiO₂ content of 70 mole % or less and the AlO_{1.5}/SiO₂ mole ratio of 3/1 or less.

2. Region of Transparent PbTiO₃ Glass-Ceramics

Glass-ceramics obtained from the clear and partially devitrified glasses in the PbO·TiO₂-AlO_{1.5}-SiO₂ system by the method described in II.2.(a) were all opaque. When treated by the method described in II.2.(b), however, some of the glasses could be transformed into transparent glass-ceramics. Their compositions (Glasses 4–6) are listed in Table I, being plotted in Fig. 1. The temperatures given in parentheses in Table I are those to which the glass specimens heated, at a rate of 48°C/hr, were transparent, although they had already crystallized. The photograph

Table I. Transparency of Various Glasses Crystallized by Heating at a Rate of 48°C/hr

Glass	Composition (mol %)			Transparency
	PbO·TiO ₂	AlO _{1.5}	SiO ₂	
1	66.6		33.4	Opaque
2	66.6	6.7	26.7	Opaque
3	66.6	13.4	20.0	Opaque
4	66.6	16.7	16.7	Transparent (650°–710°C)
5	66.6	20.0	13.4	Transparent (650°–770°C)
6	66.6	23.4	10.0	Transparent (650°–860°C)

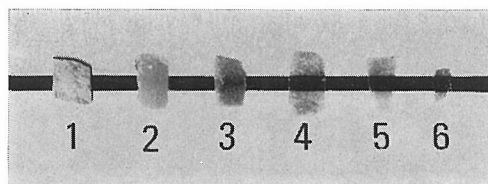


Fig. 2. Transparency of glasses 1-6 after crystallized by heating to 650°C at a rate of 48°C/hr

in Fig. 2 shows transparency of glasses 1-6 all heated to 650°C at a rate of 48°C/hr. The crystals precipitated in the transparent specimens were only the PbTiO_3 crystals of a perovskite-type. From the results shown in Figs. 1 and 2, and Table I, it is concluded that the compositions from which the transparent glass-ceramics are obtained lie in a region with a $\text{PbO} \cdot \text{TiO}_2 / (\text{SiO}_2 + \text{AlO}_{1.5})$ mol ratio of 2 or near-by and $\text{AlO}_{1.5} / \text{SiO}_2$ mole ratio of 1 to 2.3.

Layton *et al.*¹¹ concluded that composites consisting primarily of titanates or niobates with a perovskite-type structure and formed by crystallization from glass are transparent, provided that the network-former content of the parent glass is very low. The results of the present study show that their conclusion is applicable to the present $\text{PbO} \cdot \text{TiO}_2$ - $\text{AlO}_{1.5}$ - SiO_2 system, but only to its restricted region with a $\text{AlO}_{1.5} / \text{SiO}_2$ mole ratio of 1-2.3; it does not apply to the above system containing no or a small amount of $\text{AlO}_{1.5}$. For obtaining transparent glass-ceramics from the glasses of the present system, the condition found by Layton *et al.* is not satisfactory. Another condition that the $\text{AlO}_{1.5}$ content of the parent glass is $1 \leq \text{AlO}_{1.5} / \text{SiO}_2$ must be satisfied additionally.

3. Crystallization Process of Glasses

Figure 3 presents the data on the variations of the content of the crystals in glasses 1 and 4 with temperature when the glasses were heated from room temperature at a rate of 48°C/hr. Glass 4 is the glass containing $\text{AlO}_{1.5}$ from which a transparent glass-ceramic was obtained, and glass 1 is the glass containing no $\text{AlO}_{1.5}$ from which an opaque glass-ceramic was obtained. The variation of the grain size of the crystals precipitated in glass 4 with temperature was also shown in Fig. 3. The content of the crystals and the grain size were both determined by the X-ray diffraction techniques described above.

In glass 4, the PbTiO_3 crystals of a perovskite-type first precipitated from about 590°C, and their amount increased rapidly from 0 to 63 wt% in the range from 590° to 650°C, reaching 74 wt% already at 710°C. The grain size of the crystals was extraordinarily small, less than about 20 nm, which is small enough to minimize light-scattering in the glass. The transparency of the specimens heated to temperatures below 710°C (Table I) is attributed to this small size of the crystals precipitated. When the glass was heated over 710°C, the crystals grew larger and hence the glass became turbid gradually. At 950°C, their size reached the limit over which the X-ray diffraction technique could not be applied any more; that is, about 100 nm in diameter.

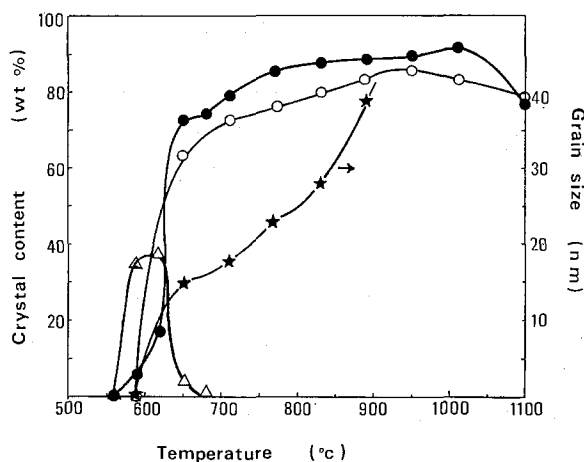


Fig. 3. Variations of crystal content and crystal grain size with temperature.

- △—△ Content of pyrochlore-type lead titanate in glass 1.
- Content of perovskite-type PbTiO_3 in glass 1.
- Content of perovskite-type PbTiO_3 in glass 4.
- ★—★ Grain size of perovskite-type PbTiO_3 in glass 4.

In glass I, metastable lead titanate crystals of a pyrochlore-type first precipitated from about 560°C . From 620° to 680°C , their amount decreased, and, at their expense, PbTiO_3 crystals of a perovskite-type newly formed, which suggests that the crystals of a pyrochlore-type transformed into those of a perovskite-type in this temperature range. The amount of the crystals of the perovskite-type increased with temperature, reaching a maximum at 1000°C . The grain size of the crystal of a pyrochlore-type first formed was so large already at the early stage of their precipitation that it could not be determined by the X-ray diffraction technique, that is, over 100 nm in diameter. This means that the crystals grew rapidly from a small number of crystal nuclei in the glass at an early stage of the crystal precipitation. The glass specimen thus became opaque as soon as the crystals began to precipitate. At the time of the transformation from the crystals of a pyrochlore-type to those of a perovskite-type, the large grain size of the former crystals was succeeded by the latter, and thus, the specimen remained opaque after the transformation.

From the difference in crystallization process between glasses 1 and 4, it is concluded that the addition of the $\text{AlO}_{1.5}$ in replacement of the SiO_2 in glass promotes the PbTiO_3 crystals of a perovskite-type to precipitate directly from the glass by accelerating their nucleation rate, thus suppressing formation of the metastable crystals.

In an earlier study on the PbO 40, TiO_2 25, SiO_2 35 mol% glass and PbO 40, TiO_2 25, Al_2O_3 10, SiO_2 25 mol% glass, the present authors found the similar function of the Al_2O_3 as described above.⁷⁾ They also found for these two glasses that the addition of the Al_2O_3 induced a glassy two-phase separation in glass prior to the precipitation of the PbTiO_3 crystals of a perovskite-type and the nucleation rate

of the crystals was accelerated by the glassy two-phase separation.⁷⁾ Since the compositions of the two glasses investigated earlier had a $\text{PbTiO}_3/(\text{PbO} + \text{SiO}_2 + \text{AlO}_{1.5})$ mole ratio of 0.4–0.5, it was unable to obtain transparent glass-ceramics from these two glasses by any heat treatment. The reason why the glass-ceramic obtained from glass 4 showed transparency is that the composition of the glass is with a high $\text{AlO}_{1.5}/\text{SiO}_2$ mole ratio together with a high $\text{PbO} \cdot \text{TiO}_2/(\text{SiO}_2 + \text{AlO}_{1.5})$ mole ratio as defined in the preceding section. Electronmicroscopic study on glass 4, made additionally in the present work, revealed that a glassy two-phase separation also occurred in glass 4 prior to the precipitation of the PbTiO_3 crystals of a perovskite-type: The phase-separated glass structure was very fine, that is, on the 16–18 nm scale, and the size of the PbTiO_3 crystals subsequently precipitated was almost the same as the heterogeneity of the phase-separated glass, that is, about 16 nm.

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